PB84-124940

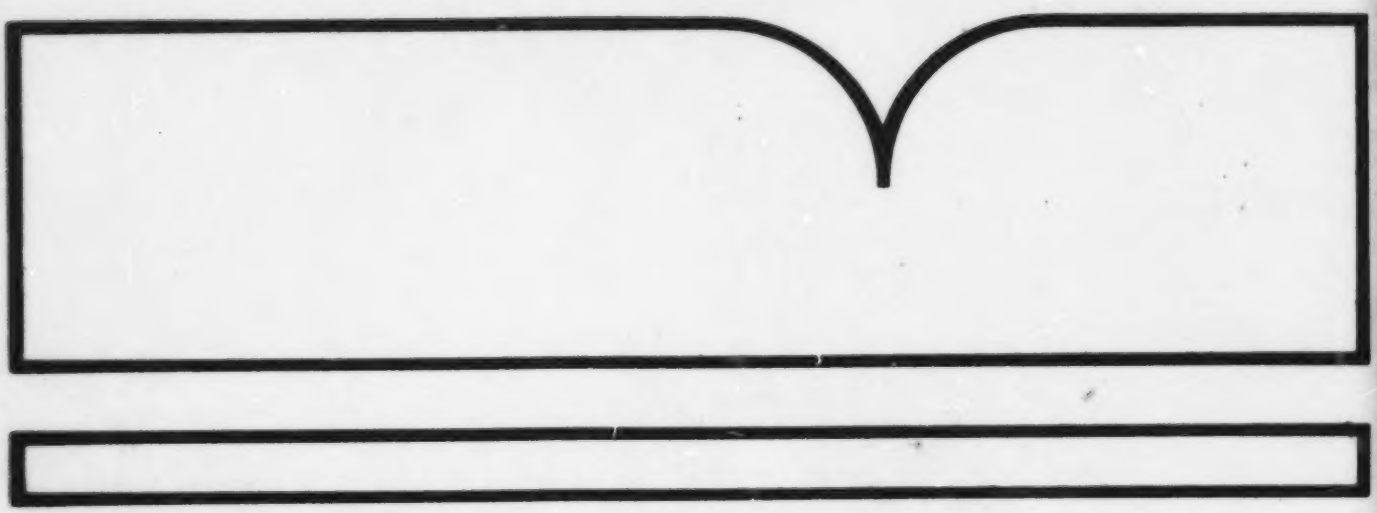
# Effect of Snowmelt on the Water Quality of Filson Creek and Omaday Lake Northeastern Minnesota

(U.S.) Geological Survey, St. Paul, MN

Prepared for

Environmental Research Lab.-Duluth, MN

1981



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| 1. REPORT NO. | 2. | 3. |
|---|---|---|
| EPA-600/J-81-661 | | PB84-124940 |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| The Effect of Snowmelt on the Water Quality of Filson Creek and Omaday Lake, Northeastern Minnesota (Journal Version) | 1981 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) D.I. Siegel | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Geological Survey St. Paul, Minnesota 55101 | 10. PROGRAM ELEMENT NO. |
| | 11. CONTRACT/GRANT NO. EPA 80DF072-01 |
| 12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Research Laboratory-Duluth 6201 Congdon Boulevard Duluth, Minnesota 55804 | 13. TYPE OF REPORT AND PERIOD COVERED |
| | 14. SPONSORING AGENCY CODE EPA/600/03 |

15. SUPPLEMENTARY NOTES
Water Resources Research 17(1): 238-242 (1981)

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS (This Report) | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 7 |
| | 20. SECURITY CLASS (This page) UNCLASSIFIED | 22. PRICE |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION

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EPA-600/J-81-661
JOURNAL ARTICLE

WATER RESOURCES RESEARCH, VOL. 17, NO. 1, PAGES 238-242, FEBRUARY 1981

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# The Effect of Snowmelt on the Water Quality of Filson Creek and Omaday Lake, Northeastern Minnesota

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Sulfate concentration and *p*H were determined in surface water, groundwater, and precipitation samples collected in the Filson Creek watershed to evaluate the sources of sulfate in Filson Creek. During and immediately after snowmelt, sulfate concentrations in Filson Creek increased from about 2 to 14 mg/l. Concurrently, $H^+$ ion activity increased from an average of $10^{-4.6}$ to $10^{-5.5}$. These changes suggest that sulfate acidity is concentrated in the snowpack at snowmelt, which is similar to changes reported in Scandinavia in areas subject to acid precipitation. Mass balance calculations indicate that the sulfate contribution from groundwater during snowmelt was minimal in comparison to that from snow. During base flow, sulfate did not appreciably increase from the headwaters of Filson Creek to the mouth, even though sulfate was as high as 58 mg/l in groundwater discharging to the creek from surficial materials overlying a sulfide-bearing mineralized zone in the lower third of the watershed. Approximately 10.6 kg of sulfate per hectare per year was retained in 1977.

## INTRODUCTION

Acid precipitation caused by the oxidation and hydrolysis of $SO_x$ and $NO_x$ emissions from the combustion of fossil fuels has lowered the *p*H of poorly buffered surface waters in Canada [*Beamish*, 1976], Scandinavia [*Braekke*, 1976], and the Adirondack Mountains of New York [*Schofield*, 1976]. Acidification of poorly buffered surface waters results in reduced diversity and abundance of fish, zooplankton, benthos, phytoplankton, and aquatic macrophytes [*Gorham*, 1976].

Acid precipitation especially impacts surface water quality at snowmelt. *Gjessing et al.* [1976], *Haapala et al.* [1975], and *Henrikson and Wright* [1977] found that fractionation and concentration of pollutants in the snowpack during the early phases of snowmelt caused large decreases in the *p*H of surface waters in Scandinavia. *Johannessen and Henrikson* [1978], and *Johannessen et al.* [1975] found from field and experimental studies in Norway that the concentrations of major cations and anions, $H^+$ ions, and heavy metals were from 3 to 5 times higher in the first fractions of meltwater than in the bulk snowpack.

Lakes and streams in northeastern Minnesota are also poorly buffered and receive precipitation having a *p*H commonly less than 5.2 [*Eisenreich*, 1978; *Gorham*, 1976]. The purpose of this paper is to report observed increases in sulfate and $H^+$ ion concentrations in Filson Creek and Omaday Lake (Figure 1) during the spring of 1977.

## SETTING

Filson Creek watershed is approximately 13 km southeast of Ely, Minnesota (Figure 1). It was chosen for study because previous data were available on the vegetation, geology, and soils and because discharge data are available for the creek near its mouth [*U.S. Geological Survey*, 1977, 1978].

Filson Creek drains 25.2 $km^2$ and flows north and west to the Kawishiwi River. Included in the watershed are Omaday and Bogberry lakes and one tributary, designated South Filson Creek for this study. South Filson has a 6.3-$km^2$ drainage area and no significant lakes.

About 60% of Filson Creek watershed is covered by mixed upland forest, 30% by wetlands and lakes, and the remainder by planted or natural stands of pine. Wetlands surround the lakes.

The bedrock is mostly troctolite (a pyroxene-poor, calcic gabbro) and other igneous rocks of the Duluth Complex (Figure 2 [*Green et al.*, 1966]). The northern 10% of the watershed is underlain by the Giants Range granite. A mineralized zone along the contact between the granite and the Duluth Complex contains copper and nickel sulfide minerals. The watershed has no carbonate rocks. Bedrock is at the land surface in about 10% of the watershed.

Most of the watershed is covered by drift generally less than 1 m thick [*Prettyman*, 1976; *Stark*, 1977; *Olcott and Siegel*, 1978]. Its mineral composition reflects the underlying bedrock types. The total thickness of drift and peat under the wetlands can exceed 15 m. The peat in most of the wetlands is fibric, herbaceous, and partly decomposed (sapric) below about 0.75 m.

## SAMPLING AND LABORATORY METHODS

Hydrologic and water quality data were collected to monitor changes in the concentration of sulfate and *p*H and to calculate a net chemical balance for sulfate. Instrumentation and sampling sites are shown in Figure 3.

Samples were taken at four locations along Filson Creek, at Omaday Lake, and at the mouth of South Filson Creek. Depth-integrated samples were not taken, because the creek is shallow and its water is well mixed. Omaday Lake was sampled at a depth of 1 m about 6 m from the north shore. Filson Creek was sampled (1) between Omaday and Bogberry lakes (F6), (2) near the mouth of Omaday Lake (F4), and (3) both immediately upstream from (F3) and within (F1) the mineralized zone to determine if changes in *p*H and concentrations of sulfate in the creek were uniform and to determine if oxidation of sulfide minerals significantly affects creek water quality. Because there is no mineralized bedrock in the watershed of South Filson, variations in *p*H and sulfate in South Filson watershed provide an 'internal control' to evaluate the effects of sulfide oxidation on the water quality of Filson Creek.

Samples of groundwater from peat were collected from four piezometers set about 1 m below the land surface in wetlands to compare sulfate and $H^+$ ion concentrations to concentra-

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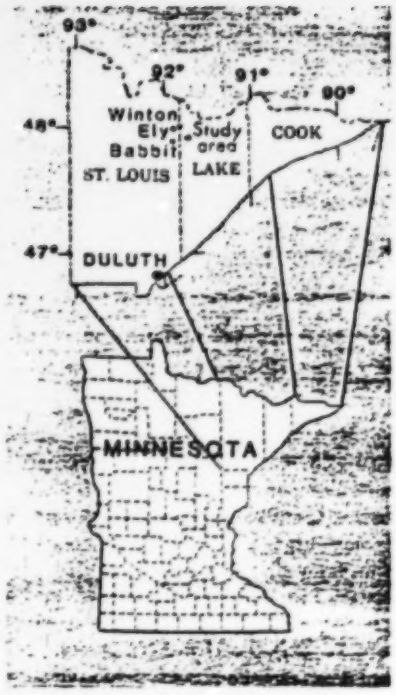



Fig. 1. Location of study area.

tions in the creek. Water quality data are available for water from deeper surficial materials around Filson Creek [*Siegel and Erickson*, 1980].

Bulk precipitation was sampled approximately biweekly at three locations. Samples were collected in 1-liter bottles mounted with two 15-cm-diameter funnels separated by Whatman 40 filter paper to remove insects and other debris from the sample. Three cores of the snowpack were collected during early March at each of four snow-sampling sites (Figure 3) and composited for analysis.

Interflow water that passed through the soil A horizon was collected biweekly at six locations to determine if $H^+$ ions or sulfate were being leached from the forest floor. Samples were collected by PVC troughs which drained to liter bottles. The troughs were covered with fine nylon mesh, which removed large particulate material from the sample.

Data on stream discharge, precipitation, and snow moisture were available from monitoring by Federal agencies. Moisture content of the snowpack was determined along snow courses run by the U.S. Forest Service. Discharge near the mouth of Filson Creek was measured by a U.S. Geological Survey recording gage. Precipitation was measured by the Forest Service at a recording rain gage about 5 km northwest of the study area until October 1977, when the gage was discontinued. After October, precipitation was assumed to be approximately equal to the average recorded by the National Weather Service at Winton and Babbit, Minnesota (Figure 1).

All sample bottles used were made of high-density polyethylene washed in 10% nitric acid and thoroughly rinsed with deionized water before sampling.

Measurements of *p*H were made in the field with a Radiometer 51 field *p*H meter or in the laboratory within 2 hours after sample collection if the air temperature was less than 0°C. Sulfate was determined by the turbidimetric method [*American Public Health Association*, 1974]. Turbidity was measured by a Beckman model 21 spectrophotometer at a wavelength of 410 Å. Color blanks were run for all samples. (Brand names used in this report are for identification only; they do not imply endorsement by the U.S. Geological Survey.)

## Results and Discussion

### *Hydrology*

Filson Creek generally responds quickly to runoff from storms once the thin till and peat cover is saturated. Flood hydrographs generally peak within 1 day of significant rainfall but recede more slowly because of drainage from surface water storage in the lakes and wetlands. Base flow is sustained mainly by discharge from surface storage. Groundwater discharge is minimal, because dense, crystalline bedrock is near the land surface and herbaceous, partly decomposed peat in the wetlands below about 1 m has low hydraulic conductivity. Hydraulic conductivities of peat similar to that in Filson Creek watershed range from only $10^{-4}$ to $10^{-3}$ cm/s [*Boelter*, 1966], which is at least 2 orders of magnitude less than the hydraulic conductivity of typical sand and gravel aquifers.

The flow of Filson Creek in the spring of 1977 was small because of drought (Figure 4). Maximum discharge was only 0.1 $m^3/s$, compared with 3.2 $m^3/s$ in 1976. Most of the snowmelt and concurrent precipitation went into temporary storage. The water content of the snowpack in early March was 50 ± 3 mm (J. Ramquist, oral communication, 1977). During March and April there was an additional 27.9 mm of precipitation. Total streamflow in March and April was equivalent to 10 mm. The difference of about 67.9 mm between total precipitation and streamflow provides a rough estimate of the storage deficit in soil moisture, wetlands, depressions, and lakes, assuming negligible evapotranspiration during early spring.

### *Water Quality*

The water quality of Filson Creek and Omaday Lake is typical of the dilute surface water in streams and lakes located on

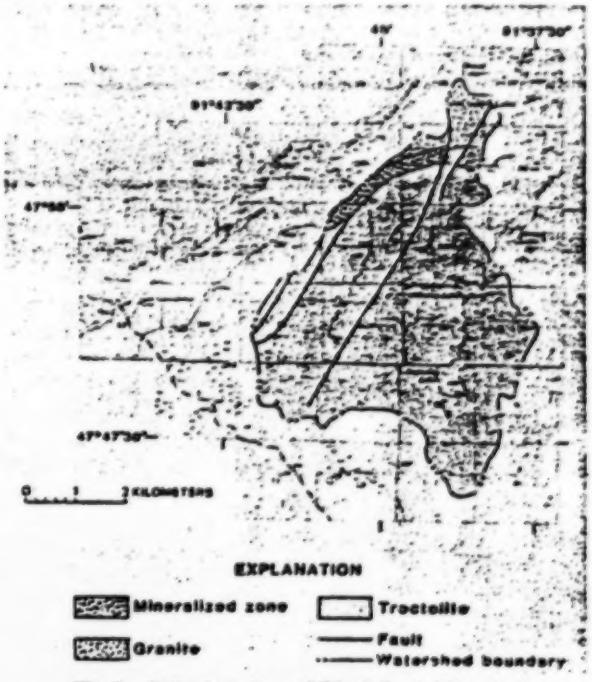



Fig. 2. Bedrock geology of Filson Creek Watershed.

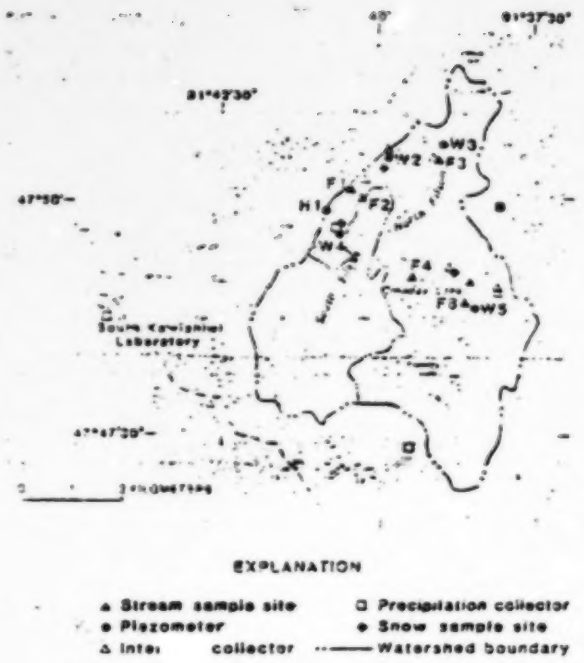



Fig. 3. Location of instrumentation and sample sites.

the Duluth Complex. Major cations are calcium and magnesium (Table 1), and the major anion is bicarbonate. As in wetland watersheds elsewhere in the state [*Verry*, 1975], organic acids contribute significantly to the anion content of the water.

Variations in the concentrations of $H^+$ ion and sulfate during snowmelt were generally similar in Filson Creek and Omaday Lake. From late April to early May, sulfate increased from about 2 to 14 mg/l at Omaday Lake and near the mouths of Filson (F1) and South Filson (F2) creeks (Figure 5). Concurrently, *p*H decreased about 1.1 units. At the wetland sites the decrease in *p*H and increase in sulfate either did not occur (F6) or were not as great (F3).

TABLE 1. Water Quality of Filson Creek (Site F1) and Omaday Lake During Base Flow Conditions, January 29, 1978

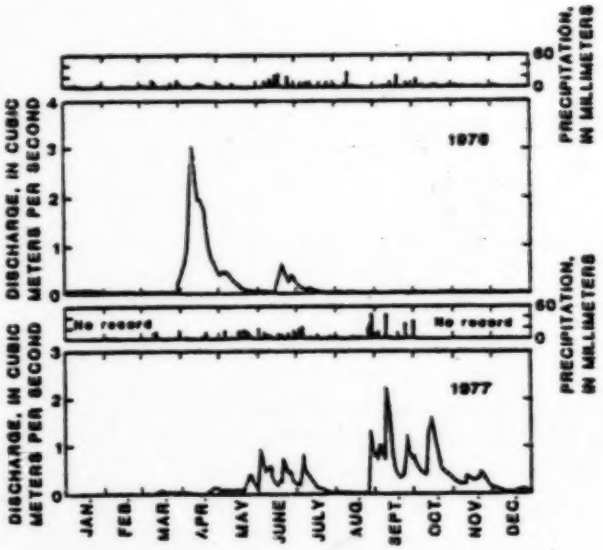
| | Filson Creek | Omaday Lake |
|---|---|---|
| *p*H | 6.20 | 6.18 |
| Calcium | 3.3 | 3.9 |
| Sodium | 1.7 | 1.8 |
| Magnesium | 1.6 | 1.5 |
| Potassium | 0.4 | 0.4 |
| Sulfate | <2.0 | <2.0 |
| Bicarbonate | 13.0 | 8.0 |
| Chloride | 1.9 | 2.2 |
| Silica | 15.5 | 14.7 |

Concentrations are in milligrams per liter. Cations were determined from samples filtered through 0.45-μm filters. Data are from D. I. Siegel (unpublished data, 1978).

Sulfate in groundwater in wetlands is highest near the mineralized zone. Mean concentrations of sulfate in wetland piezometers W2 and W3, located in the mineralized zone, were 46 and 17 mg/l, compared with mean concentrations of 7 and 9 mg/l in wells W4 and W5, located about 0.4 and 4.8 km, respectively, away from the mineralized zone. The *p*H in groundwater in the wetlands averaged less than 6.0, generally lower than in the creek. On a yearly basis, variations in the concentration of $H^+$ ion in wetland groundwater are not correlated ($r = -0.03$) to variations in the concentration of sulfate (Figure 6), probably because of organic acids, which contribute to the *p*H.

Sulfate concentrations in groundwater in drift are also greater close to the mineralized bedrock. For example, the concentration of sulfate from a well in drift above the mineralized bedrock was over 100 mg/l in both February and April 1976 [*U.S. Geological Survey*, 1977].

Sulfate and *p*H values in bulk precipitation from April to October 1977 were similar to those in interflow water through the soil A horizon. Sulfate in bulk precipitation ranged from 5.8 to less than 1 mg/l, whereas the *p*H of precipitation ranged from 4.2 to 6.3. The *p*H and concentration of sulfate in the



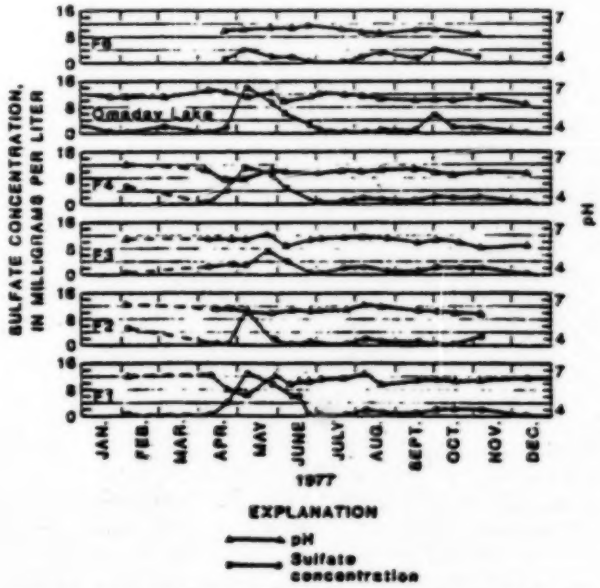




Fig. 5. Concentration of sulfate and *p*H in Filson Creek and Omaday Lake, 1977. (Note that the dashed parts of the curves denote

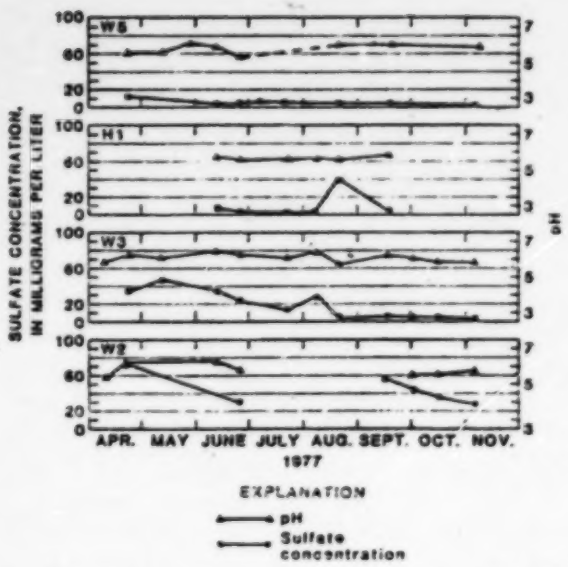



Fig. 6. Concentration of sulfate and *p*H in wetland piezometers, 1977.

composite snow sample collected in March 1977 were 4.7 and 2 mg/l, respectively. Concentrations of sulfate and $H^+$ ion activity in precipitation are not well correlated ($r = -0.39$). Some error probably occurred in the analyses for sulfate at concentrations less than 2 mg/l [*American Public Health Association*, 1974]. Nitric acid may contribute significantly to precipitation acidity but was not evaluated in this study. Sulfate in interflow water ranged from 3.3 to less than 1 mg/l, and *p*H ranged from 4.5 to 6.4. Statistical analysis (Student *t*-test at 0.01 level of significance) indicates that $H^+$ ion activity in 24 samples of interflow water was similar to that in 16 samples of precipitation. Mean concentrations of sulfate in both precipitation and interflow water were less than 2 mg/l. Both the *p*H and the sulfate data indicate that decomposition of organic matter on the forest floor contributes little additional sulfate or acidity to Filson Creek.

Variations in the concentration of sulfate and *p*H in Filson Creek and Omaday Lake can be related to the response of the watershed to hydrologic conditions in 1976–1977 and to a probable concentration of sulfate acidity in the early stages of snowmelt. The concentration of sulfate in Filson Creek and Omaday Lake rose and peaked before major storms in late May 1977 (Figure 5). This suggests either a concentration mechanism for sulfate in the snowpack or discharge to the creek of groundwater with a high concentration of sulfate. High concentrations of sulfate in groundwater are found only near the mineralized zone. Consequently, if groundwater discharge were significant, the concentrations of sulfate at South Filson and Omaday Lake could not have increased from groundwater discharge, because their drainage areas contain no mineralized bedrock.

Mass balance calculations indicate that the amount of groundwater that conservatively might have discharged to the creek is at least an order of magnitude too small to increase the concentration of sulfate in Filson Creek from 2 to 15 mg/l. The calculations assumed (1) two-dimensional groundwater flow from the wetlands to the creek, (2) a hydraulic conductivity of the peat ranging from $10^{-4}$ to $10^{-3}$ cm/s [*Boelter*, 1969], (3) hydraulic gradients ranging from 0.9 to 3.7 m/km [*Siegel and Erickson*, 1980; *Stark*, 1977], (4) a saturated peat thickness of 0.6 m discharging groundwater to the creek, and (5) groundwater discharge occurring along the entire length of the creek.

Calculations were done by Darcy's law and indicate that total groundwater discharge to the creek probably ranges from $3 \times 10^{-4}$ to $3 \times 10^{-3}$ m³/s. The largest concentration of sulfate in the creek in May was coincident with a streamflow of 0.1 m³/s. Assuming the maximum estimated groundwater discharge, the concentration of sulfate in groundwater would have had to be at least 400 mg/l to cause the observed increase in sulfate in the creek. This value is about an order of magnitude greater than the maximum sulfate concentration determined in groundwater except in drift immediately over the mineralized bedrock. It is not similar to sulfate concentrations in groundwater from wetlands in the headwaters of the creek or to concentration of sulfate generally found in groundwater from the drift. In addition, during base flow conditions, sulfate did not appreciably increase from the headwaters of Filson Creek to the mouth, even though sulfate was as great as 58 mg/l in groundwater discharging to the creek from wetlands over the mineralized zone.

The amount of sulfate deposited by snow and precipitation from November 1976 to March 31, 1977, should be equal to the amount of sulfate transported by the creek during March to early May. The sum of the sulfate deposition from November 1976 to March 31, 1977, is, in fact, about equal to the sulfate discharged by the creek in April and May (Figure 7). About 2.0 kg/ha of sulfate was transported from Filson Creek

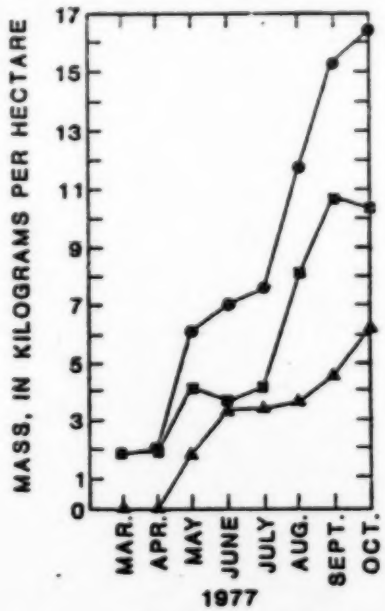



Fig. 7. Cumulative deposition and loss of sulfate from March 1976 through October 1977. (Note that the March data include precipitation from November 1976 to March 31, 1977.)

watershed in April and May 1977, compared to about 1.3 kg/ha deposited by precipitation from November 1976 through March 1977.

Concentrations of sulfate, however, did not correlate well with increases in $H^+$ ion activity ($r = 0.38$). At some locations (e.g., F4 and F3) the increase in $H^+$ ion activity lagged slightly behind the increase in sulfate concentrations (Figure 5). The lack of correlation could also be the result of $H^+$ ion buffering by silicate minerals in the till, sorption of $H^+$ ions by colloidal material, and sorption of sulfate by soil sesquioxides.

It seems that the watershed retained as much as 10.6 kg/ha of sulfate (Figure 7) from November 1976 through October 1977. About 16.9 kg/ha of sulfate was deposited by precipitation, whereas only about 6.3 kg/ha was lost by stream discharge. Reducing conditions likely developed in the decomposing peat in the wetlands once saturation was reached after the drought. Some sulfate would be reduced and precipitated with iron or other metals. The odor of hydrogen sulfide was noted at Filson Creek locations F6 and F3, located in wetlands, which indicates some sulfate reduction and loss from the system as hydrogen sulfide. Also, sulfate could be retained in the watershed by sorption onto sesquioxides in the till [*Johnson*, 1980; *Johnson et al.*, 1979].

## SUMMARY AND CONCLUSIONS

Variations in the amount of sulfate and hydrogen ion in Filson Creek suggest that sulfate acidity is concentrated in early spring snowmelt. Sulfate increased from about 2 to 14 mg/l, and $H^+$ ion activity increased from $10^{-4.6}$ to $10^{-3.5}$. These changes were delayed about 2 weeks after the initial snowmelt period, because snowmelt first infiltrated into dry soils and wetlands. Groundwater discharge from wetlands to the creek was calculated to be $3 \times 10^{-3}$ m$^3$/s. Because of the small groundwater discharge, sulfate did not appreciably increase in the creek at base flow from headwater locations downstream, even though there was as much as 53 mg/l of sulfate in groundwater directly over a mineralized zone near the mouth of the creek. Filson Creek watershed seemed to retain about 10.6 kg/ha of sulfate during the study. Sulfate was probably reduced and precipitated as metallic sulfides in wetlands and also sorbed onto the till.

*Acknowledgments.* This study was made possible by grants from the Minnesota Geological Survey and Graduate School of the University of Minnesota. I wish to express special appreciation to H. O. Pfannkuch for helpful advice and encouragement during the study and to M. Edens and D. Pollock for assistance in the fieldwork.

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(Received January 9, 1980;
revised July 29, 1980;
accepted August 7, 1980.)